# CATHODE PROCESSES OF HYDROGEN EVOLUTION ON VANADIUM-CONTAINING MATERIALS

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Electrode processes on vanadium-containing materials in aqueous alkaline media for hydrogen synthesis have been studied. The titanium alloys (VT-1, VT-6), chrome vanadium steel (12Cr1MoV), carbon steel 45, steel 45 coated by nickel and steel 45 coated by vanadium-doped nickel were examined. According to the cathodic stationary polarization dependencies, the hydrogen evolution overvoltage on these electrode materials was analyzed. The linear part of the hydrogen overvoltage dependencies on current density logarithms is revealed, which indicates the hydrogen ion reduction limited by charge transfer stage. The impurities of vanadium compounds in 12Cr1MoV steel and VT-6 titanium alloy reduce the hydrogen overvoltage by 120-150 mV, which indicates the electrocatalytic activity of these alloys in cathodic reactions in alkaline solutions. Vanadium-containing electrodes show high stability and corrosion resistance during long-term operation. Their application in the technology of hydrogen electrosynthesis is promising.

An important problem of modern hydrogen energetics is the expansion of hydrogen production by electrolysis.

The most effective factor for such expansion is the use of catalytically active electrode materials and alloys, which have depolarizing properties in cathodic reactions under electrolysis of alkaline solution. The catalytic activity of cathode materials affects the hydrogen evolution overvoltage and determines the kinetic parameters of the whole cathodic reaction. In the state-of-the-art electrolysis of alkaline solutions, carbon steels, platinoids, tungsten and molybdenum carbides and some nickel, cobalt and tungsten alloys are used as active cathode materials [1-5]. The intensive development of hydrogen energetics with the use of electrochemical methods requires the study and application of new materials that can reduce the material and energy costs of electrolysis, for example, using complex cycles of anodic depolarization with electroaccumulating compounds.

Analysis of literature data and research indicate that vanadium and titanium alloys, ferrovanadium, chrome vanadium alloys and vanadium-doped nickel coatings possess electrocatalytic properties.

The aim of the work is to compare the catalytic activity of surfaces of iron and titanium alloys with surfaces containing alloying vanadium compounds in reaction of hydrogen evolution. Particularly, chromium-molybdenum-vanadium steel consisting of α-Fe and some inclusions of chromium, molybdenum and vanadium carbides [6] is of interest.

**Research methodology**

Kinetic parameters of the cathodic reduction of hydrogen ions were determined for 12Cr1MoV vanadium steel (the content of V is 0,3%), VT-6 titanium-vanadium alloy (the content of V 4,5%), nickel and nickel doped with vanadium compounds coatings on steel 45 as well as for steel 45 and titanium VT-1, not containing vanadium in its composition. Kinetic characteristics on the mentioned cathodes were determined based on the study of cathode reactions in 1M NaOH solution.

Stationary polarization dependencies were obtained by cathodic polarization using programmable source of current "BVP 15V 15A timer/ampere" and digital voltmeter SCH68009. The calculations of hydrogen overvoltage and Tafel equation coefficients were performed based on the analysis of these dependences.

**Results and discussion**

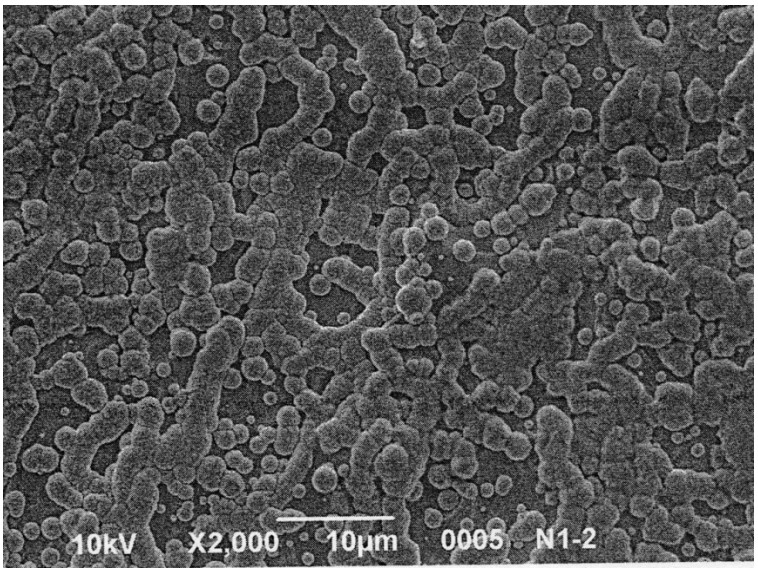
Figure 1 presents the surface morphology of vanadium-doped nickel coating obtained on steel surface. The coatings were formed as spherical globule, which is typical for electrolytic nickel [7, 8], with an arbitrary filling surface.

Figure 2 shows the dependencies of hydrogen evolution overvoltage on current density on modified steel materials in semilogarithmic coordinates. There are lineal regions at the curves under the current density $J_k = 10^{-4,5}...10^{-2}$ that obey Tafel equation with the values of coefficients «a» = - 0.44 ... - 0.64 V, and «b» = 0.061 ...0.113.

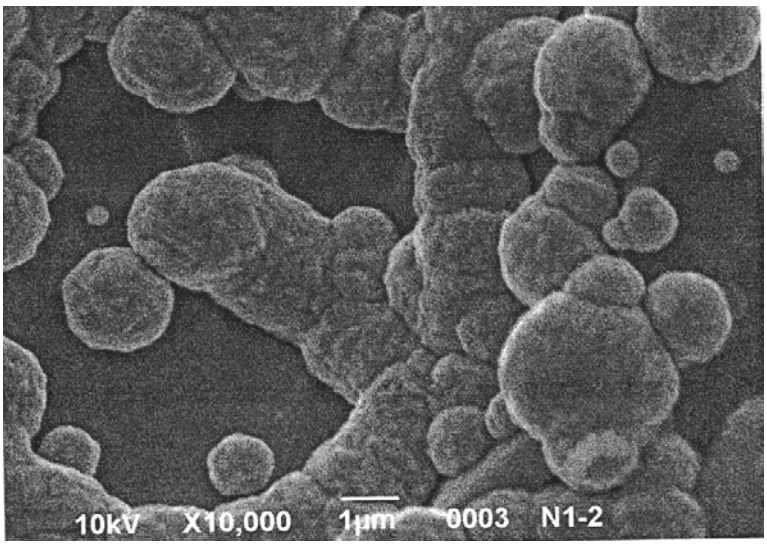
Table 1 shows equations corresponding to the linear regions of stationary cathode polarization dependencies on the studied electrodes of modified steel and titanium alloys, VT-1 and VT-6, containing up to 5.3% of vanadium (Table. 1).

Analysis of the data in the table shows that the values of hydrogen overvoltage on steel electrodes without vanadium additions are higher, then the overvoltage on materials containing vanadium dopants (compare samples №1 and №3, №2 and №4). The values of exchange current are $(0.065…3.971)\cdot10^{-6}$ A/cm$^2$. The slope b of linear fragments of the curves is close to 0.118, which indicates the limiting of proton reduction by difficulties at the charge transfer stage. The hydrogen evolution overpotential on titanium alloys is higher compared to steels due to the alloy nature and surface condition. However, hydrogen overvoltage on alloy VT-6 is lower than the overvoltage on VT-1 alloy.

A decrease in the cathodic polarization on the vanadium- containing materials is caused by their ability to possess the electrocatalytic properties, associated with the higher mobility of charged particles in reduction reactions.




a




b

**Fig. 1.** The surface morphology of nickel coatings. Magnification:
a – x 2000, b – x 10 000

Chrome-vanadium steel (12Cr1MoV) shows improved corrosion resistance in neutral and alkaline media in a wide range of temperatures and pressures. It is used in chemical technology and energy. The use of this steel in membrane electrolysis of water can greatly simplify the electrosynthesis of hydrogen. Steel electrode materials with vanadium-doped nickel coating are also promising. The use of such coating decreases the electrolysis voltage by 120-150 mV and improves stability of the electrolyzers operation due to the higher chemical stability in alkaline environments.

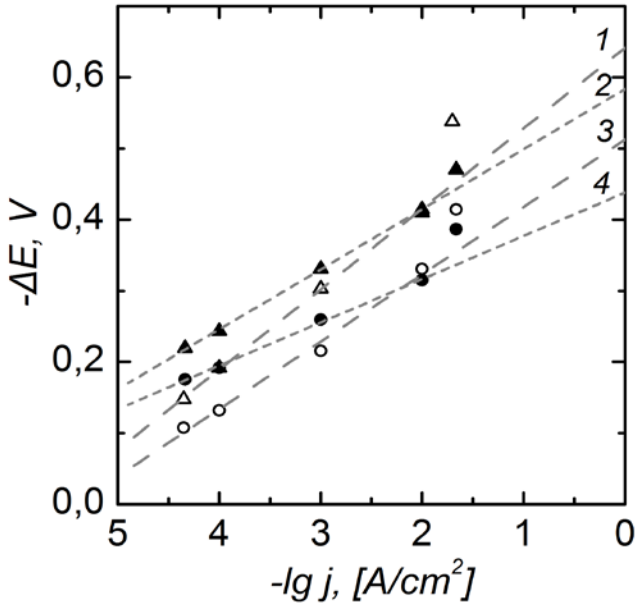



**Fig. 2**. Semilogarithmic dependencies of hydrogen evaluation overvoltage on current density in 1M NaOH at the cathode materials (t = 25 °C): 1 – steel 45; 2 – steel 45 coated by nickel; 3 - 12Cr1MoV steel; 4 – steel 45 coated by vanadium-doped nickel

**Table 1.** The kinetic characteristics of cathode materials

| № | Cathode material | Dopant | Tafel equation | -η, V (i=1 A/dm$^2$) | $i_o \cdot 10^{-6}$, A/cm$^2$ |
|---|---|---|---|---|---|
| 1 | Steel 45 | Cr <0.25 Ni <0.25* | - η = 0.64 + 0.113 lg i | 0.415 | 2.139 |
| 2. | Steel 45 / Ni | - | - η = 0.58 + 0.083 lg i | 0.41 | 0.108 |
| 3 | Steel (12Cr1MoV) | V 0.15÷0.30 Cr 0.9÷1.2** | - η = 0.51 + 0.095 lg i | 0.33 | 3.971 |
| 4 | Steel 45 / Ni, V | V | - η = 0.44 + 0.061 lg i | 0.31 | 0.065 |
| 5 | Titanium VT-1 | Fe <0.25 *** | - η = 0.88 + 0.15 lg i | 0.58 | 1.380 |
| 6 | Titanium VT-6 | V 3.5÷5.3**** | - η = 0.62 + 0.13 lg i | 0.36 | 17.224 |

Chemical composition of the alloys:

* Steel 45: C 0.42 - 0.5; Si 0.17 - 0.37; Mn 0.5 - 0.8; Ni <0.25; S <0.04; P <0.035; Cr <0.25; Cu <0.25; As <0.08; Fe ~ 97;

** Steel (12Cr1MoV): C 0.08 - 0.15; Si 0.17 - 0.37; Mn 0.4 - 0.7; Ni <0.3; S <0.025; P <0.03; Cr 0.9 - 1.2; Mo 0.25 - 0.35; V 0.15 - 0.30; Cu <0.2; Fe ~ 96;

*** VT-1: Fe <0.25; C <0.07; Si <0.1; N <0.04; Ti 99.24 - 99.7; O <0.2; H <0.01;

**** VT-6: Fe <0.6; C <0.1; Si <0.1; V 3.5 - 5.3; N <0.05; Ti 86.45 - 90.9; Al 5.3 - 6.8; Zr <0.3; O <0.2; H <0.015.

## Conclusions

The study of kinetic characteristics of vanadium steel (12Cr1MoV) and carbon steel 45 coated by vanadium-doped nickel in 1M NaOH solution showed that at the cathodic current densities ranging from $10^{-4}$ to$10^{-2}$ A/cm$^2$ the hydrogen reduction mechanism is mainly determined by the charge transfer overvoltage.

A decrease in hydrogen evolution overvoltage on vanadium-containing materials is determined to be caused by catalytic activity of vanadium compounds.

The advantage and possibility to reduce the energy consumption for alkaline water electrolysis for hydrogen electrosynthesis using vanadium-containing steel and titanium materials, particularly using metallic anode depolarization cycles, was shown.

## References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